Japanese Kokai Patent Application No. Sho 60[1985]-239743

RECORDING MEDIUM

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[There are no amendments to this patent.]

Claim

A recording medium in which a monomolecular film or a cumulative monomolecular film comprising a host molecule having a hydrophilic group, a hydrophobic group, and an enclosure group, and a guest molecule enclosed in the above-mentioned host molecule, is produced on a carrier to form a recording layer, and the complex composition ratio of the above-mentioned host

molecule and guest molecule is not an equimolar ratio in a
practical sense.

Detailed explanation of the invention

(1) Field of the technology

The present invention pertains to a recording medium in
which recording is performed by utilizing the chemical change or
physical change of a monomolecular film consisting of an
enclosure complex or cumulative monomolecular film layer.

(2) Background of the technology

A variety of recording mediums having an organic compound as
a recording layer are known.

For example, an optical recording medium in which a
thin-film organic compound is used as a recording layer is
disclosed in, for example, Japanese Kokai Patent Application No.
Sho 56[1981]-16948 and Japanese Kokai Patent Application No.
Sho 58[1983]-125246. In each case, it pertains to a laser
recording medium in which an organic colorant is used as the
recording layer, and recording and playback are achieved with a
laser beam. In particular, the medium disclosed in Japanese Kokai
Patent Application No. Sho 58[1983]-125246 has a recording layer
consisting of a thin film of a cyanine dye indicated by (I)
below.

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General formula (I)
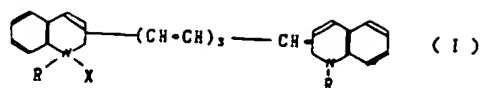
The cyanine dye indicated by chemical structure (I) is coated onto a plastic base to form a thickness of 1000 Å or less, for example, a thickness of approximately 300 Å, by means of a rotary coating machine, and a thin film is produced. When the distribution of the molecular orientation within the film is random, optical scattering occurs within the film when photoradiation is applied, and the degree of chemical reaction that occurs upon application of each type of radiation varies on a microscopic level. For this reason, a recording medium with a uniform molecular distribution and orientation within the film is desirable, and a reduced film thickness is required for increased recording density. However, when a coating method is used, the limitation in the thickness of the film is approximately 300 Å, and random molecular distribution and orientation within the film was difficult to achieve.

It is stated in Japanese Kokai Patent Application No. Sho 56[1981]-42229 and Japanese Kokai Patent Application No. Sho 56[1981]-43220 that a cumulative film of diacetylene compound with a high light quantum effect [sic; possibly, quantum yield] and high resolution suggested as a resist material can be applied to thin-film electrooptical devices, electroacoustic devices, piezopyroelectric devices, etc., as well as resist materials.

Recently, an improvement in the method of manufacturing diacetylene compound cumulative film has been disclosed in Japanese Kokai Patent Application No. Sho 58[1983]-111029. The

diacetylene compound cumulative film produced on a base by the method described in the above-mentioned invention undergoes polymerization upon application of ultraviolet [radiation] and produces a diacetylene compound polymer film, or masking is used and ultraviolet [radiation] is applied to perform a partial polymerization and the nonpolymerized portion is removed to produce a pattern, and the result is used as a thin-film optical device or integrated circuit element.

However, all of the above-mentioned methods are limited to diacetylene compounds, and the possibility of erasing the recording when used as a thin-film optical device is not discussed at all.

Meanwhile, as a means to eliminate the above-mentioned problems, an optical recording medium that can be used repeatedly is produced by forming a recording layer consisting of a monomolecular film or monomolecular cumulative film comprised of at least a photopolymeric monomer containing a hydrophilic, a hydrophobic, and at least one unsaturated bond in the molecule on a base and is disclosed in Japanese Patent Application No. Sho 58[1983]-190932.

In all of the above-mentioned diacetylene compound cumulative films and monomolecular films or monomolecular cumulative films comprised of a photopolymeric monomer, a method of manufacturing in which a hydrophilic and hydrophobic group are introduced to the photoreactive compound, which is deposited directly on a base, is used. As a result, it is difficult to produce films with various functions using a simple method, and a reduction in the photoreactivity of the film results from introduction of the hydrophilic group and hydrophobic group.

Furthermore, to control the molecular orientation within the film, which is very important for high-density recording, a very complex operation is required.

In an effort to eliminate the above-mentioned problems in the conventional technology, and as a result of their research on 1) a method of producing a variety of functional films using a relatively simple method, 2) a method in which the above-mentioned film formation is carried out in such a manner that the properties of the functional molecule are not reduced even when a reduced film is used, and 3) a method in which orientation of the film molecular structure is performed in the in-plane direction of the film to provide a high orientation without a special operation, thereby, the present invention was accomplished. Furthermore, it was easily possible to produce a high-quality recording medium with high sensitivity and high resolution using the above-mentioned method.

(3) Disclosure of the invention

The objective of the present invention is to produce a high-density recording medium capable of chemical or physical changes on the molecular level based on extrinsic properties.

Also, the objective is to produce a superior medium regarding the molecular orientation within the plane of the medium which is an important factor for high-density recording at the molecular level than those produced by conventional methods. Furthermore, the objective is to produce a medium with a variety of properties through a relatively simple change in the operation during production of the above-mentioned recording medium.

The above-mentioned objectives of the present invention can be achieved by the present invention described below.

A recording medium in which a monomolecular film or a monomolecular layer cumulative film comprised of a host molecule having a hydrophilic group, a hydrophobic group, and a group whereby inclusion (enclosure complex) of other molecules is made possible (host molecule), and a different type of molecule enclosed by a host molecule (guest molecule) is produced on a carrier to form a recording layer, and the composition ratio of the above-mentioned host molecule and guest molecule is not an equimolar ratio in a practical sense.

The material that comprises the recording layer of the present invention consists of two types of molecules, a molecule having at least one group containing a hydrophilic group, a hydrophobic group, and a group whereby inclusion of a different molecule is made possible (which is referred to as the host molecule), and a different type of molecule enclosed in the above-mentioned host molecule (which is referred to as the guest molecule). When the monomolecular film, or cumulative monomolecular film layer of the enclosure complex made of the above-mentioned host molecule and guest molecule is deposited onto a carrier, the recording medium of the present invention can be produced. Between the above-mentioned two types of molecules, it is necessary for one or both of them to change either chemically or physically based on external factors such as light, heat, electrical energy, or magnetic fields. In other words, in the recording medium of the present invention, recording is carried out utilizing the above-mentioned chemical change or physical change.

The host molecule that can be used in the present invention, as described above, is a molecule having a hydrophilic group, a hydrophobic group, and a group capable of forming at least one enclosure complex with a different type of molecule, and capable of forming an enclosure complex that is not equimolar with respect to the guest molecule in a practical sense. As typical examples of structural elements capable of forming the hydrophilic group or hydrophobic group within the molecule, a variety of commonly known hydrophilic groups and hydrophobic groups can be mentioned. The group capable of forming an enclosure complex with a different type of molecule can be produced by introduction of hydroxy groups, carbonyl groups, carboxyl groups, ester groups, amino groups, nitrile groups, thiol groups, imino groups, etc. In the following, the above-mentioned host molecule is explained in specific terms using a host molecule having hydroxy groups indicated by general formulas (IIb)-(IIc) as examples.
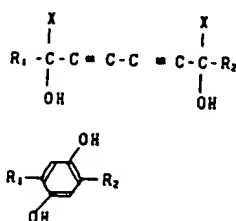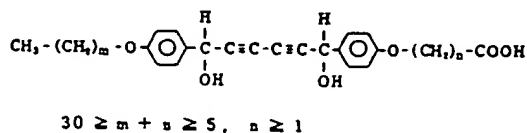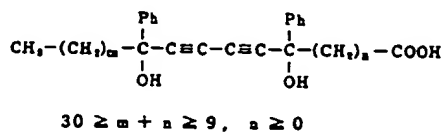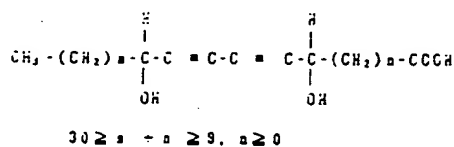

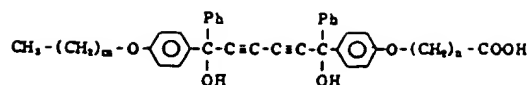(In this case, X = H or C_6H_5.)

In other words, having a hydrophilic group and hydrophobic group within the molecule means, for example, in the above-mentioned chemical structure, a hydrophilic group exists on

either R_1 or R_2, and a hydrophobic group exists on the other, or both R_1 and R_2 exhibit hydrophilic properties or hydrophobic properties in relation to groups other than those two. Regarding the structure of R_1 and R_2, when a hydrophobic group is to be introduced, a long-chain alkyl group with 5-30 carbon atoms is especially suitable, and when a hydrophilic group is to be introduced, a fatty acid with 1-30 carbon atoms is especially suitable.
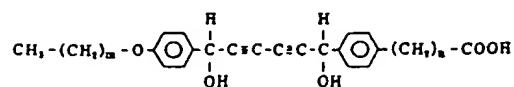
For specific examples of the host molecule used in the present invention, diacetylene diol derivatives (Nos. 7-12, Nos. 22-27), hydroquinone derivatives (Nos. 13-15, Nos. 18-30), etc., can be mentioned as suitable examples. It should be noted that in the following, m and n each represent a positive integer, Z represents $-CH_3$ or $-COOH$, and Ph represents $-C_6H_5$.

[Examples of diacetylene diols]

$$CH_3-(CH_2)_m-\underset{\underset{OH}{|}}{\overset{\overset{Z}{|}}{C}}-C \equiv C-C \equiv C-\underset{\underset{OH}{|}}{\overset{\overset{Z}{|}}{C}}-(CH_2)_n-COOH$$

$$30 \geq m + n \geq 9, \quad n \geq 0$$

$$CH_3-(CH_2)_m-\underset{\underset{OH}{|}}{\overset{\overset{Ph}{|}}{C}}-C \equiv C-C \equiv C-\underset{\underset{OH}{|}}{\overset{\overset{Ph}{|}}{C}}-(CH_2)_n-COOH$$

$$30 \geq m + n \geq 9, \quad n \geq 0$$

$$CH_3-(CH_2)_m-O-\langle O \rangle-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-C \equiv C-C \equiv C-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\langle O \rangle-O-(CH_2)_n-COOH$$

$$30 \geq m + n \geq 5, \quad n \geq 1$$

$$CH_3-(CH_2)_m-O-\langle O \rangle-\overset{Ph}{\underset{OH}{C}}-C\equiv C-C\equiv C-\overset{Ph}{\underset{OH}{C}}-\langle O \rangle-O-(CH_2)_n-COOH$$

$$30 \geq m + n \geq 5, \quad n \geq 1$$

$$CH_3-(CH_2)_m-O-\langle O \rangle-\overset{H}{\underset{OH}{C}}-C\equiv C-C\equiv C-\overset{H}{\underset{OH}{C}}-\langle O \rangle-(CH_2)_n-COOH$$

$$30 \geq m + n \geq 5, \quad n \geq 0$$

$$CH_3-(CH_2)_m-O-\langle O \rangle-\overset{Ph}{\underset{OH}{C}}-C\equiv C-C\equiv C-\overset{Ph}{\underset{OH}{C}}-\langle O \rangle-(CH_2)_n-COOH$$
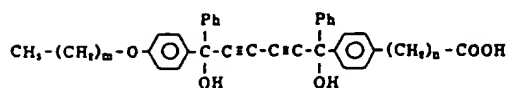
$$30 \geq m + n \geq 5, \quad n \geq 0$$

[Examples of hydroquinone derivatives]

$$CH_3-(CH_2)_m-\langle O \rangle\overset{OH}{\underset{OH}{}}-(CH_2)_n-COOH$$

$$30 \geq m + n \geq 13, \quad n \geq 0$$

$$CH_3-(CH_2)_m-O-\langle O \rangle\overset{OH}{\underset{OH}{\langle O \rangle}}\langle O \rangle-O-(CH_2)_n-COOH$$

$$CH_3-(CH_2)_m-O-\langle O \rangle\overset{OH}{\underset{OH}{\langle O \rangle}}\langle O \rangle-(CH_2)_n-COOH$$
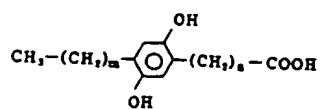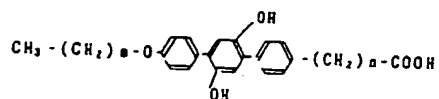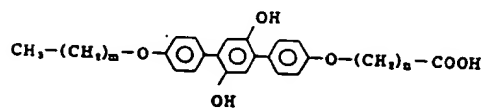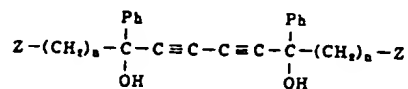
$$30 \geq m + n \geq 9, \quad n \geq 0$$

[Examples of diacetylene diol derivatives]*

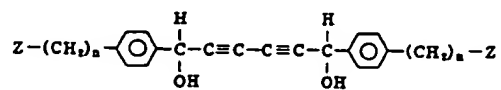$$Z-(CH_2)_a-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C\equiv C-C\equiv C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-(CH_2)_a-Z$$

$$30 \geq a \geq 3$$

$$Z-(CH_2)_a-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C\equiv C-C\equiv C-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-(CH_2)_a-Z$$

$$30 \geq a \geq 3$$

$$Z-(CH_2)_a-O-\bigcirc-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C\equiv C-C\equiv C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\bigcirc-O-(CH_2)_a-Z$$

$$30 \geq a \geq 1$$

$$Z-(CH_2)_a-O-\bigcirc-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C\equiv C-C\equiv C-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\bigcirc-O-(CH_2)_a-Z$$

$$30 \geq a \geq 1$$

$$Z-(CH_2)_a-\bigcirc-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C\equiv C-C\equiv C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\bigcirc-(CH_2)_a-Z$$

$$30 \geq a \geq 1$$

$$Z-(CH_2)_a-\bigcirc-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-C\equiv C-C\equiv C-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-\bigcirc-(CH_2)_a-Z$$
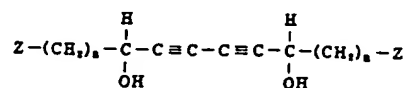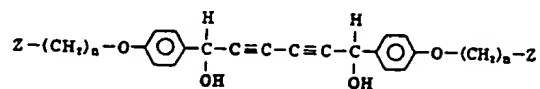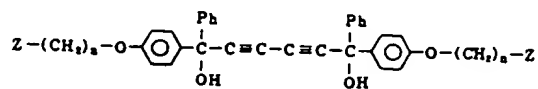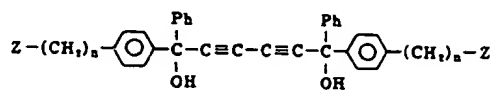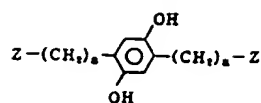
$$30 \geq a \geq 1$$

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*[Editor's note: compound Nos. 16-21 not present in original.]

[Examples of hydroquinone derivatives]

$$Z-(CH_2)_n-\overset{\displaystyle OH}{\underset{\displaystyle OH}{\bigcirc}}-(CH_2)_n-Z$$

$30 \geq n \geq 5$

$$Z-(CH_2)_n-O-\bigcirc-\overset{\displaystyle OH}{\underset{\displaystyle HO}{\bigcirc}}-\bigcirc-O-(CH_2)_n-Z$$

$30 \geq n \geq 1$

$$Z-(CH_2)_n-\bigcirc-\overset{\displaystyle OH}{\underset{\displaystyle OH}{\bigcirc}}-\bigcirc-(CH_2)_n-Z$$
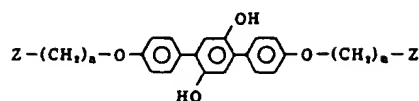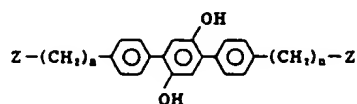
$30 \geq n \geq 1$

With the exception of substitution of a long-chain alkyl group or long-chain carboxylic acid for the host molecule, and introducing hydrophilic properties or hydrophobic properties, the above-mentioned compounds themselves are known compounds; furthermore, formation of a crystalline enclosure complex of the host molecule that is not modified with a long-chain alkyl group, etc., is also described in the Journal of the Chemical Society of Japan, No. 2, pp. 239-242 (1983).
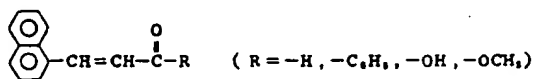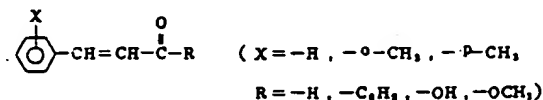
For the guest molecule capable of producing an enclosure complex with the above-mentioned host molecules, in general, molecules capable of forming a strong hydrogen bond with the host molecule are desirable. For this reason, as described above, when the host molecule has a hydroxy group as the enclosure group,

aldehyde, ketone, amine, sulfoxide, etc., can be mentioned as guest molecules. Furthermore, for guest molecules, different types of halogen compounds, or π-electron compounds, in other words, alkene, alkyne, arene, etc., can be selected. In either case, a molecule having a structure that makes it possible for the enclosure complex produced to have a desired image formation ability [is selected].
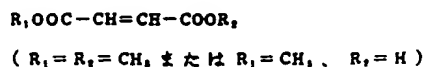
In the following, specific examples of guest molecules with different functions are shown.

(1) For specific examples of guest molecules that can be used for an optical recording medium that utilizes the dimerization reaction of the guest molecule, olefin compounds (Nos. 31-34), diolefin compounds (Nos. 35-38), anthracene derivatives (No. 39), 2-aminopyridinium (No. 41), etc., can be mentioned.
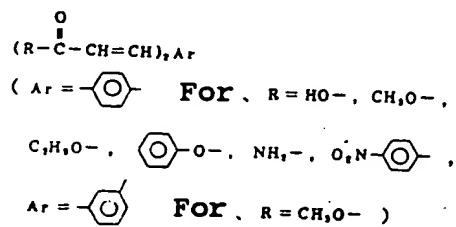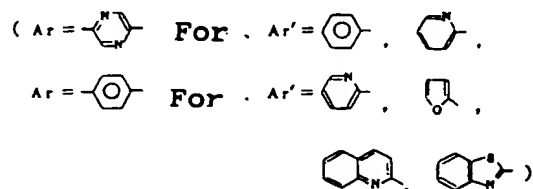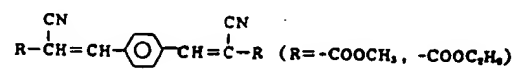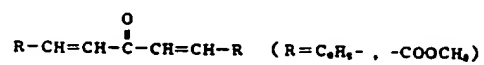
[Examples of olefin compounds]

$$\text{(X = -H, -o-CH}_3\text{, -p-CH}_3$$
$$\text{R = -H, -C}_6\text{H}_5\text{, -OH, -OCH}_3\text{)}$$

$$\text{(R = -H, -C}_6\text{H}_5\text{, -OH, -OCH}_3\text{)}$$

$$\text{NC-CH=CH-CN}$$

Key: 1   or

$$\text{R}_1\text{OOC-CH=CH-COOR}_2$$
$$\text{(R}_1 = \text{R}_2 = \text{CH}_3 \text{ または R}_1 = \text{CH}_3\text{, R}_2 = \text{H)}$$
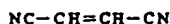
①

[Examples of diolefin compounds]

(Ar = ⟨N⟩ For . Ar' = ⟨O⟩ , ⟨N⟩ .

Ar = ⟨O⟩ For . Ar' = ⟨N⟩ , ⟨O⟩ ,

⟨quinoline⟩ , ⟨benzimidazole⟩)

$$(R-\overset{O}{\underset{\|}{C}}-CH=CH)_2 Ar$$

(Ar = ⟨O⟩ For . R = HO− , $CH_3O−$,

$C_2H_5O−$, ⟨O⟩−O− , $NH_2−$, $O_2N−$⟨O⟩ ,

Ar = ⟨O⟩ For . R = $CH_3O−$)

No. 37

$$R-\overset{CN}{\underset{|}{C}}H=CH-\langle O\rangle-CH=\overset{CN}{\underset{|}{C}}-R \quad (R=-COOCH_3, -COOC_2H_5)$$

No. 38

$$R-CH=CH-\overset{O}{\underset{\|}{C}}-CH=CH-R \quad (R=C_6H_5-, -COOCH_3)$$

[Examples of anthracene derivatives]

(R = CH₃⁻ , CHO- , -COOC₂H₅ .. Br⁻)
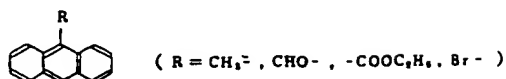
[Examples of acrydinium derivatives]

· X⁻   (R = -H , -CH₃ , -C₂H₅ ,

X⁻= I⁻ , Br⁻ , Cl⁻)

[2-aminopyridinium]

· X⁻   (X⁻ = Cl⁻ , Br⁻ , I⁻)
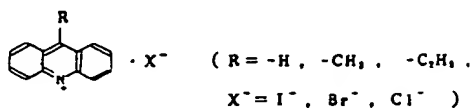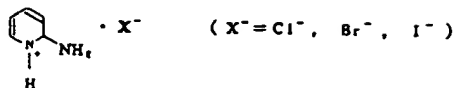
(2) For specific examples of guest molecules that can be used for a recording medium that utilizes sublimation of the guest molecule, ketones (No. 42), epoxides such as 1,2-epoxypropane (No. 43), ethylenimine (No. 44), benzene (No. 45), chlorides such as dichloromethane and chloroform (Nos. 46, 47), bromides such as methyl bromide (No. 48),

(R = -CH₃ , -C₂H₅)

$$CH_2Cl_2,$$

$$CHCl_3,$$

$$CH_3Br$$
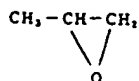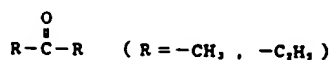
etc., can be mentioned.

As a method of producing the monomolecular film or cumulative monomolecular film layer of the enclosure complex comprised of above-mentioned host molecules and guest molecules, for example, the Langmuir-Blodgett (LB method) developed by I. Langmuir et al. can be used. The LB method is a method in which a monomolecular film or cumulative film of the monomolecular layer is produced by utilizing the tendency of molecules to form a monomolecular layer on the surface of water with the hydrophilic group facing downward when an appropriate balance is retained in a molecular structure having a hydrophilic group and hydrophobic group in the molecule (that is, balance of the two properties). The monomolecular layer on the surface of the water is a two-dimensional system. When the molecules are distributed at random and form a "gaseous film", the equation of a two-dimensional ideal gas can be established between surface area A and the surface pressure π per molecule, $\pi A = kT$.
In this case, k is Boltzmann's constant and T is the absolute temperature. When A is adequately reduced, the intramolecular interaction increases and forms a "condensed film" (or solid film) consisting of a two-dimensional solid material. The condensed film can be transferred to the surface of a carrier comprised of a different material or having a different shape such as a glass base, one layer at a time. As a specific example

of the method of producing the monomolecular film (which is referred to as a complex monomolecular film), or complex monomolecular cumulative film of the host molecule that includes the guest molecule of the present invention, five methods A-E shown below can be mentioned.

(A) The host molecule and the guest molecule of the target enclosure complex are dissolved in a solvent. [The enclosure complex] is then formed in an aqueous phase and the enclosure complex is precipitated in the form of a film. In this case, when the structure of the host molecule includes a hydrophilic group (carboxyl group) and a hydrophobic group (alkyl group) on both ends of the molecule as indicated by compounds Nos. 1-15, the enclosure complex precipitated on the aqueous phase is developed on the aqueous phase with the hydrophilic group of the host molecule facing the aqueous phase regardless of the hydrophilic and hydrophobic properties of the guest molecule. On the other hand, when the host molecule takes on the structure indicated by compounds Nos. 16-30, $Z = -CH_3$, wherein both ends of the molecule consist of only hydrophobic groups, the enclosure complex develops on the aqueous phase with the hydrophilic group of the guest molecule facing the aqueous phase as indicated by Figure 4. Also, for $Z = -COOH$, wherein both ends of the molecule consist only of hydrophilic groups, the enclosure complex develops on the aqueous phase with the hydrophilic group of the host molecule facing the aqueous phase as indicated by Figure 5.

Subsequently, a partition board (or a float) is provided so that spreading of the precipitate on the aqueous phase does not occur freely, the area of spread is restricted, the state of

spreading of the film material is controlled, and the surface pressure π in proportion to the state of spreading is obtained. The partition board is then moved, the area of spread is reduced, the state of spread the film material is controlled, the surface pressure is slowly increased, and a surface pressure π suitable for production of the cumulative film can be obtained. The surface pressure is retained, the cleaned carrier is carefully placed in vertical motion, and the complex monomolecular film is transferred to the carrier. The complex monomolecular film is produced as described above, the above-mentioned operation is repeated, and a complex monomolecular cumulative film layer with a desired degree of buildup can be produced.

In order to transfer the monomolecular layer onto the surface of the carrier, in addition to the above-mentioned dipping method, the horizontal adsorption method, rotational cylinder method, etc., can be mentioned. The horizontal adsorption method is a method in which the carrier is brought into contact with the surface of the water horizontally and transfer is performed, and the rotational cylinder method is a method in which a cylindrical carrier is rotated on the surface of the water, and the monomolecular layer is transferred to the surface of the carrier. In the above-mentioned vertical dipping method, a monomolecular layer with the hydrophilic group of the host molecule facing the carrier side can be produced when a carrier with a surface having hydrophilic properties is pulled out of the water in a direction that crosses the surface of the water. When the carrier is transported in the vertical direction as described above, a single monomolecular layer is built up for each process. The position of the film molecules produced is

reversed in the removal process and dipping process, therefore, when the above-mentioned method is used, a Y-type film, in which the hydrophilic group and hydrophilic group of the host molecule and the hydrophobic group and hydrophobic group of the host molecule face each other between the layers, can be produced. On the other hand, in the horizontal adsorption method, the carrier is brought into contact with the surface of the water, transfer is performed, and a complex monomolecular layer with the hydrophobic group of the host molecule facing the carrier side can be produced on the carrier. In said method, a change in the direction of the film molecules produced does not occur even when built up, and an X-type film, in which the hydrophobic group faces the carrier in all layers, can be produced. A cumulative film, in which the hydrophilic group is facing the carrier side in all layers, is referred to as a Z-type film.

In the rotational cylinder method, a cylindrical carrier is rotated on the surface of the water, and the monomolecular layer is transferred to the surface of the carrier. Transferring the monomolecular layer onto the carrier is not limited to the above-mentioned methods, and when a carrier with a large surface area is used, a method in which the carrier is extruded into the aqueous phase from a carrier roll, etc., can be used as well. Also, the orientation of the hydrophilic group or hydrophobic group facing the carrier described above is a rule, a surface treatment can be provided for the carrier, and the direction can be changed.

In the above-mentioned film formation process, control of the orientation in the in-plane direction of the film material has been mainly controlled through adjustment of the surface

pressure in the past, but it has been very difficult to achieve a highly ordered orientation unless the film material is a compound with a very simple structure, for example, a straight-chain fatty acid, etc. However, in the present invention, an enclosure complex is used as a film material. Thus, a film with a highly ordered orientation can be produced relatively easily. In other words, configurations between the host molecule-guest molecule, host molecule-host molecule, and guest molecule-guest molecule are defined at the point where the enclosure complex is precipitated on the aqueous phase based on the hydrogen bonds, van der Waals forces, etc., and the host molecule and guest molecule are arranged with a crystal lattice order. Also, when only the guest molecule has functionality, chemical modification for the guest molecule, in other words, introduction of hydrophobic group or hydrophilic group, is not performed. Thus, reduction in the functionality accompanied by film formation does not occur.

(B) A guest molecule that exhibits solubility is dissolved in the aqueous phase. Subsequently, a host molecule is dissolved with a solvent and spread onto the aqueous phase. In this case, formation of the enclosure complex takes place among the host molecule-guest molecule at the same time, and formation of a film takes place. The combination of the host molecule and guest molecule and the film formation method that follows are based on the methods described in (A).

(C) A guest molecule that exhibits solubility is dissolved in the aqueous phase. Subsequently, the host molecules and guest molecules of the target enclosure complex are dissolved in a solvent and spread onto the aqueous phase. The combination of

host molecule and guest molecule and the film formation method that follows are based on the method described in (A).

(D) A host molecule is dissolved in a solvent and spread onto the aqueous phase. Subsequently, a closed-system device is used and the side of the gaseous phase, that is, the space inside the device, is formed into a gas atmosphere of the guest molecule. In this case, the guest molecule on the gaseous phase side is enclosed at the same time, and an enclosure complex is precipitated in a form of a film. The above-mentioned method is especially effective for compounds in which the guest molecule has a low boiling point and is likely to vaporize, for example, acetone, etc. The combination of the host molecule and guest molecule and the film formation method that follows are based on the method described in (A).

(E) A closed-system device is used and the side of the gaseous phase, that is, the space inside the device, is filled with a gaseous atmosphere comprised of the guest molecule. Then, the host molecule and guest molecule of the target enclosure complex are dissolved in a solvent. It is then sprayed onto the aqueous phase, and an enclosure complex is precipitated in the form of a film. The combination of the host molecule and guest molecule and the film formation method that follows are based on the method described in (A).
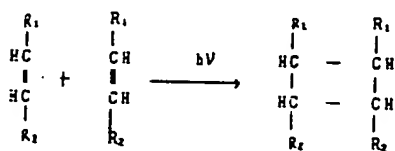
The complex monomolecular film and complex monomolecular cumulative film produced on the carrier using the above-mentioned methods have a high density and highly ordered orientation, and when a recording layer is made with the above-mentioned films, a recording medium having good characteristics as a high-density, high-resolution recording medium that can be used for optical

recording, thermal recording, electrical recording, magnetic recording, etc., can be produced.

When the complex monomolecular film and complex monomolecular cumulative film produced above are used as the recording layer of a recording medium, a variety of recording methods, as described below, are conceivable.

1. Optical recording medium that utilizes the photodimerization reaction of the guest molecule

For example, when one of Nos. 7-15 or Nos. 22-30 is used for the host molecule, and a guest molecule having a photodimerizable double bond such as those indicated by Nos. 31-38 are used in combination, an enclosure complex having a host molecule and guest molecule composition ratio (mole ratio) of 1:2 can be produced. When the energy required to achieve polymerization such as gamma rays, X-rays, or ultraviolet [radiation] is applied to the above-mentioned complex monomolecular film or complex monomolecular layer cumulative film according to a specified pattern, dimerization takes place between the guest molecules in the irradiated areas, as indicated by equation III.

$$
\begin{array}{cccccc}
R_1 & & R_1 & & R_1 & R_1 \\
| & & | & & | & | \\
HC & & CH & & HC & - & CH \\
| & + & | & \xrightarrow{h\nu} & | & & | \\
HC & & CH & & HC & - & CH \\
| & & | & & | & | \\
R_1 & & R_2 & & R_2 & R_2
\end{array}
$$

The above-mentioned reaction can occur when the distance between adjoining unsaturated bonds is 4 Å or less, but in a complex monomolecular film or complex monomolecular layer cumulative film

produced by the above-mentioned methods, not only can the dimerization product be produced easily, but also, only one type of isomer or structure among a variety of materials that are likely to be produced at the time of the dimerization reaction can be produced. In other words, the configuration between the guest molecules in the enclosure complex layer is highly ordered. Also, depolymerization does not occur after dimerization even in the dark, and areas that are not exposed to radiation remain in the monomeric form; thus, a recording based on a specified pattern can be produced as indicated by Figure 1.

Reading of the recorded information can be done by, for example, irradiation of visible light. In other words, the conjugated system of the monomer undergoes decomposition when polymerization is performed; thus, changes occur in the absorption wavelength of the visible light. The maximum absorption wavelength shifts toward the lower wavelengths; thus, playback of the information can be achieved by reading the change in spectral absorption (Figure 2).

In addition to readout of the spectral absorption by visible light, playback can be achieved by reading the change in volume and after dimerization using the schlieren method. The above-mentioned method is especially effective for a complex monomolecular film or complex monomolecular cumulative film of a compound having a structure that exhibits a significant difference in volume at the time of polymerization and after the dimerization. Also, instead of directly forming the complex monomolecular film or complex monomolecular layer cumulative film on the base, an optically conductive layer such as Se, ZnO, and CdS can be produced on the base, and a complex monomolecular film
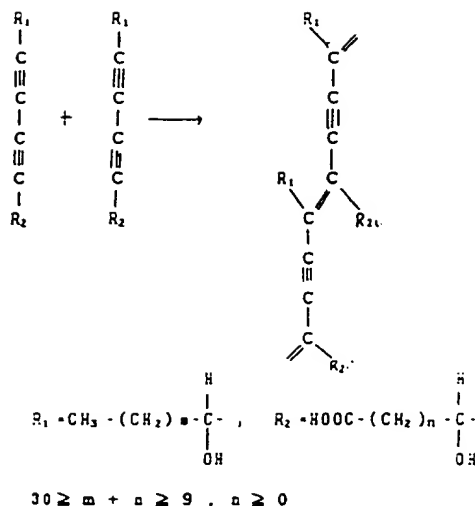
or complex monomolecular cumulative film also is produced; thus, the difference in absorption between the monomer and the dimer can be read out electronically.

The dimer has absorption at a wavelength of 270 nm based on the cyclobutane ring, and when ultraviolet [radiation] with a wavelength of 270 nm is applied, the dimer returns to the initial monomers. Thus, erasure of the recorded information is possible (Figure 3).

Also, as the guest molecule of the photodimer, a compound such as the anthracene derivatives indicated by No. 39 can be used. In this case, the photodimerization reaction progresses according to reaction equation IV.

$$2 \quad \text{[anthracene derivative]} \quad \xrightarrow{h\nu} \quad \text{[photodimer]} \qquad (\text{IV})$$
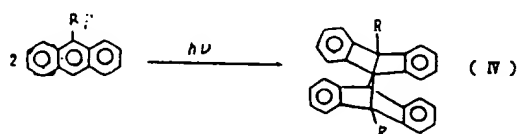
Also, when No. 7 is used as the host molecule, polymerization takes place between host molecules in the irradiated areas as indicated by equation V when the energy required for polymerization such as X-rays, gamma rays, or ultraviolet [radiation] is applied, and polydiacetylene is produced.

$$R_1 \cdot CH_3 \text{-} (CH_2)_m \text{-} \overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}} \text{-} \quad , \quad R_2 \cdot HOOC \text{-} (CH_2)_n \text{-} \overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}} \text{-}$$

$$30 \geq m + n \geq 9 \quad , \quad n \geq 0$$

Therefore, a significant increase in the adhesion with the base is made possible when a total exposure is performed for the complex monomolecular film or complex monomolecular cumulative film. In particular, a significant increase in the chemical resistance (solvent resistance) can be observed. When the above-mentioned total exposure is performed, when the guest molecule has photodimeric properties, dimerization also takes place in the guest molecule. But when the material is used as an optical recording medium, as a case opposite to the example described above, when depolymerization is performed through application of light with a wavelength at the absorption wavelength of the cyclobutane ring (ultraviolet) according to a specified pattern, recording or display can be achieved.

For the above-mentioned optical recording medium, one with a film thickness of 100-3000 Å is especially desirable.

2. Recording medium that utilizes sublimation of the guest
    molecule

For example, when one of the compounds indicated in Nos. 7-15 and Nos. 22-30 is used as the host molecule and a guest molecule such as [one of] Nos. 42-48 are used in combination, an enclosure complex with the host molecule and guest molecule composition ratio (mole ratio) of 1:2 can be produced. When a laser beam or electron beam having sufficient intensity for separation and vaporization of the guest molecule from the enclosure complex is applied to the complex monomolecular film or complex monomolecular cumulative film according to a specified pattern, the guest molecule remains enclosed in the host molecule in the area where radiation is not applied; thus, recording based on the above-mentioned pattern can be produced.

Readout of the recorded information is achieved by reading the existence of ultraviolet absorption based on the carbonyl group included in the compound when No. 42 is used as the guest molecule. Also, the change in the film before and after application of the laser beam or electron beam can be read out by the schlieren method, and said method is effective when the compounds indicated by Nos. 42-48 are used as guest molecules, as well. Also, when a complex monomolecular film or complex monomolecular cumulative film containing the compound of No. 42 is produced on the photoconductive layer such as Se, ZnO, or CdS, it is possible to electrically read out the difference in absorption between the complex enclosure group and the guest molecule group alone.

In the above-mentioned recording medium, one with a film thickness of 100-1000 Å is especially desirable.

As indicated by the principle, the method of producing the film is very simple, and it is possible to produce a recording medium with the above-mentioned superior properties at low cost.

The carrier used for production of the above-mentioned complex monomolecular film or complex monomolecular cumulative film used in the present invention is not especially limited, but when a surfactant is adsorbed on the surface of the carrier, the complex monomolecular film is disturbed when the complex monomolecular film layer is transferred from the surface of water, and a high-quality complex monomolecular film or complex monomolecular layer cumulative film cannot be produced; thus, a carrier with a clean surface is used. For examples of carriers that can be used in this case, glass, metals such as aluminum, plastics, ceramics, etc., can be mentioned.

The complex monomolecular film or complex monomolecular cumulative film formed on the carrier is firmly bonded, and peeling or delamination from the carrier hardly occurs, but in order to further increase the adhesion, an adhesive layer can be formed between the complex monomolecular film or complex monomolecular cumulative film and the carrier. Also, the adhesion can be increased through selection of the conditions of formation of the complex monomolecular film layer, for example, concentration of the hydrogen ion in the aqueous phase, type of ion used, water temperature, carrier transport speed, etc.

It is desirable to provide a protective film on the complex monomolecular film or complex monomolecular cumulative film from the standpoint of chemical stability of the complex monomolecular

film or complex monomolecular cumulative film, but depending on the type of film-forming molecule, a protective film is not a requirement.

In the following, the present invention is further explained in specific terms with application examples. Compound Nos. 49-53 are listed in Table I.

Application Example 1

An optical recording medium that utilizes the photodimerization reaction of the guest molecule (1)

Diacetylene diol indicated by No. 49 was used as a host molecule, and chalcone was used as the guest molecule. The two were dissolved in chloroform at a mole ratio of 1:2 and spread over an aqueous phase of cadmium chloride with a pH of 6.5 and concentration of 4×10^{-4}M. After removing the chloroform solvent by evaporation, the surface pressure was increased to 35 dynes/cm, and precipitation of the enclosure complex was performed in the form of a film. Subsequently, the surface pressure was kept constant, a glass board with a thoroughly clean surface having hydrophilic properties was gently moved in the vertical direction at a rate of 7 cm/min in such a manner that the board crossed the surface of the water, and a complex monomolecular film was transferred to the board. A complex monomolecular film, an optical recording medium having a recording layer comprised of a complex monomolecular film, and a complex monomolecular cumulative film formed by buildup of 3, 5,

9, 15, and 19 layers were produced. In the above-mentioned buildup process, the board was left standing for 30 min each time after being removed from the aqueous phase, and the moisture adsorbed on the board was removed by evaporation. As for the film formation machine, a Langmuir-Trough 4 produced by Joyce Corp. of England was used.

X-ray application was done for the optical recording medium produced according to a pattern, the dimerization reaction of the guest molecule indicated by equation VI was performed, and information recording was performed. A high-density recording in the ordered molecular [system] was possible.
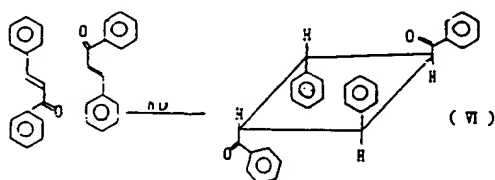
Chalcone

Playback of the recording was performed by reading out the change in absorption at a wavelength of around 380-420 nm associated with dimerization of the guest molecule. Subsequently, when ultraviolet [radiation] was applied at a wavelength of 270 nm for 1 h, depolymerization took place, and the recording was erased.

Application Examples 2-12

Instead of the chalcone described in Application Example 1, compounds indicated by Nos. 31-38 were used as guest molecules, and similar results were obtained. (Application Examples 2-9)

Furthermore, when chalcone was used as the guest molecule, and compounds indicated by Nos. 50-52 were used as host molecules, recording, playback, and furthermore, erasure of the recording were made possible as in Application Example 1. (Application Examples 10-12)

Application Examples 13-24

Optical recording medium that utilizes the photodimerization reaction of the guest molecule (2)

First, total exposure was performed for each optical recording medium described in Application Examples 1-12 using a high-pressure mercury lamp, and dimerization was performed for all of the guest molecules. Ultraviolet [radiation] with a wavelength of around 270 nm, which corresponds to the maximum absorption of the cyclobutane ring produced at the time of dimerization, was applied to the above-mentioned media to form a pattern, depolymerization of the guest molecule was carried out, and information recording was performed. Recording in the ordered molecular system was possible. Playback was accomplished by reading the change in absorption at wavelengths of approximately 380-420 nm associated with depolymerization of the guest molecule. It was confirmed that erasure of the recording, that

is, dimerization of all of the guest molecules, was possible by means of total exposure of the above-mentioned recording medium with a high-pressure mercury lamp.

Application Example 25

An optical recording medium that utilizes photodimerization of the guest molecule (3)

Diacetylene diol indicated by No. 53 was used as the host molecule, cinnamic acid was used as the guest molecule, and optical recording media with a recording layer comprised of a complex monomolecular film, and cumulative layers of 3, 5, 9, 15, and 19 layers were produced as in Application Example 1. Subsequently, total exposure was performed for above-mentioned films with a high-pressure mercury lamp, dimerization of the guest molecule (equation VII) was carried out, and polymerization of the host molecule (equation V) was carried out; subsequently, ultraviolet [radiation] with a wavelength of 270 nm was applied according to a specified pattern, depolymerization of the guest molecule was performed, and information recording was performed. Recording in the ordered molecular [system] was possible.
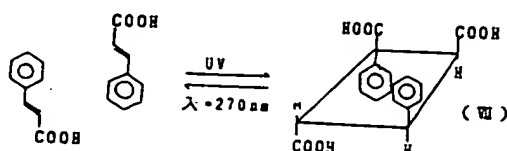
Playback was accomplished by reading the change in absorption at wavelengths of approximately 380-420 nm associated with depolymerization of the guest molecule.

Subsequently, it was confirmed that erasure of the recording was possible by means of a total exposure of the above-mentioned recording medium with a high-pressure mercury lamp. Also, the recording medium that had been totally exposed with a high-pressure mercury lamp was dipped in alcohol for approximately 30 sec and recording/playback of information was performed as described above. No problems were observed. In other words, it was confirmed that the chemical resistance of the recording medium can be increased when polymerization is performed for the host molecule.

Application Examples 26 and 27

Diacetylene diol indicated by No. 53 was used as the host molecule, and anthraldehyde was used as the guest molecule. They were dissolved in chloroform at a mole ratio of 1:2, and an optical recording media with recording layers comprised of a complex monomolecular film, and cumulative layers of 5, 9, 15, and 31 layers were produced as in Application Example 1.

Subsequently, X-ray radiation was performed on the optical recording medium produced, the dimerization indicated by equation (IV) of the guest molecule was carried out, and information recording was performed. Recording in the ordered molecular [system] was possible. Playback was performed by reading the change in absorption at wavelengths of approximately 370-390 nm associated with dimerization of the guest molecule. When

ultraviolet [radiation] with a wavelength of 313 nm was applied
for 1 h, depolymerization took place, and it was confirmed that
erasure of the recording was possible.

Similar results were obtained when the anthracene derivative
indicated by No. 41 was used. (Application Example 27)

Application Example 28

A recording medium that utilizes sublimation of the guest
molecule (1)

As a host molecule, the diacetylene diol indicated by No. 49
was dissolved in chloroform and spread onto the aqueous phase
with a pH of 6.5 and a cadmium chloride concentration of
4×10^4M. After removing the chloroform solvent by evaporation,
saturation was performed for the vapor-phase side of the system
with acetone. The surface pressure was increased to
35 dynes/nm [sic] in an atmosphere of acetone, the enclosure
complex was precipitated in the form of a film, and the acetone
in the vapor-phase side of the system was replaced with air or
nitrogen. Subsequently, a glass plate with a clean surface was
gently pulled in a vertical motion, while the surface pressure
remained constant, at a vertical rate of 2 cm/min in a direction
that crossed the surface of the water. The complex monomolecular
film was transferred onto the plate, and recording media having a
recording layer comprised of a complex monomolecular film and
complex monomolecular cumulative films having 3, 5, 9, 15, 19,
40, 60, and 80 layers were produced. In the above-mentioned

buildup process, the board was left standing for 30 min each time it was removed from the aqueous phase, and the moisture adsorbed on the board was removed by evaporation. As for the film formation machine, a Langmuir-Trough 4 produced by Joyce Corp. of England was used.

When a laser beam was applied to the recording medium produced by a carbon dioxide laser or infrared laser according to a specified pattern, the guest molecule, that is, the acetone molecule, was removed in the area radiated alone through vaporization, the intensity of the absorption spectra in that area (λ_{max} = 280 nm) was reduced, and information recording was performed. Recording in the ordered molecular [system] was possible. Also, playback of the recording through readout of the presence of the guest molecule by means of the schlieren method was possible. When the above-mentioned recording medium was left standing in an acetone stream for 1 h, enclosure of acetone took place in the area where the acetone had been removed, erasure of the recording was possible, and repeated recording was made possible. The above-mentioned process consisting of recording, erasure, and rerecording was performed at least several tens of times, and it was confirmed that the product withstood repeated use.

Application Examples 29-31

Instead of the host molecule indicated by No. 49 used in Application Example 28, the compounds indicated by Nos. 50-52

were used, and similar results to those in Application Example 28 were obtained.

Application Examples 32-37

Recording medium that utilizes sublimation of the guest molecule (2)

As host molecules, compounds indicated by Nos. 49-52 were used and were dissolved in chloroform and spread onto an aqueous phase having a pH of 6.5 and a concentration of cadmium chloride of 4×10^{-4}M. In this case, saturation was performed for the vapor-phase side of the system with chloroform. After vaporization of the chloroform of the solvent (solution side) was nearly complete (about 5 min), the surface pressure was increased to 35 dynes/cm, precipitation of the enclosure complex was performed in the form of a film, and the chloroform at the vapor-phase side was replaced with air or nitrogen. Subsequently, a glass plate with a clean surface was gently pulled in a vertical motion, while the surface pressure remained constant, at a vertical rate of 2 cm/min in a direction that crossed the surface of the water. The complex monomolecular film was transferred onto the plate, and recording media having a recording layer consisting of a complex monomolecular film and complex monomolecular cumulative films having 3, 5, 9, 15, and 19 layers were produced.

When a laser beam was applied to the recording media produced using a carbon dioxide laser or infrared laser according

to a specified pattern, removal of the guest molecule through vaporization, that is, removal of the chloroform, was observed only in the area radiated. Recording in the ordered molecular [system] was possible. Also, playback of the recording through reading of the presence of the guest molecule by means of the schlieren method was possible. When the above-mentioned recording medium was left standing in a chloroform stream for 1 h, enclosure of chloroform took place in the areas where chloroform had been removed, erasure of the recording was accomplished, and repeated recording was possible. The above-mentioned process consisting of recording, erasure, and rerecording was performed at least several tens of times, and it was confirmed that the product withstood repeated use.

Also, when benzene (No. 45, Application Example 36), and dichloromethane (No. 46, Application Example 37) were used for the guest molecule and development solvent, similar results were achieved.

Application Examples 38-43

Recording medium that utilizes sublimation of the guest molecule (3)

For host molecules, the compounds indicated by Nos. 49-52 were used, and for guest molecules, 1,2-epoxypropane (No. 43) was used. As in Application Example 26, recording media having a recording layer comprised of complex monomolecular films and complex monomolecular cumulative films were produced (Application Examples 38-41). In this case, approximately 1-10M of

1,2-epoxypropane (No. 43) was dissolved in the aqueous phase, and dispersion of the guest molecule in the vapor-phase side in the water was prevented. Methods used for recording, playback, and erasure, and the results obtained, were the same as in Application Example 28.

Also, when acetone and ethylenimine (No. 44) were used as the guest molecules, similar results were obtained. (Application Examples 42 and 43)

Application Examples 44-47

Recording medium that utilizes sublimation of the guest molecule (4)

For the host molecules, compounds indicated by Nos. 49-52 were used, and for the guest molecules, methyl bromide, No. 48 was used. Recording media having recording layers comprised of complex monomolecular films and complex monomolecular cumulative films were produced as in Application Example 26. Methods used for recording, playback, and erasure, and the results obtained, were the same as in Application Example 28.

Application Examples 48-54

Recording medium that utilizes sublimation of the guest molecule (5)

For the host molecules, compounds indicated by No. 53 were used, and for the guest molecules, compounds indicated by

Nos. 42-48 were used. A complex monomolecular film and complex monomolecular cumulative films with 3, 5, and 9 layers were produced. The method used for production of said films varied slightly depending on the type of guest molecule used, and the methods described in Application Examples 26-43 were used. Total exposure was performed for the above-mentioned complex monomolecular film and complex monomolecular cumulative films with a high-pressure mercury lamp, polymerization of the host molecule was carried out, and recording media were produced.

Methods used for recording, playback, and erasure, and the results obtained, were the same as in Application Example 26 or Application Example 28. According to the above-mentioned method, adhesion of the host molecule is higher than that of Application Examples 26-43. As a result, the chemical strength of the recording medium is increased accordingly, and it was discovered that repeated application can be increased to at least 100 times.

Table I

	基本骨格	-①)
No.49	No.10	m = 9 , n = 2
No.50	No.25	Z-COOH, n = 2
No.51	No.15	m = 9 , n = 2
No.52	No.30	Z-COOH, n = 4
No.53	No.7	m = 8 , n = 8

Key: 1   Base skeleton

Brief explanation of the figures

Figures 1-3 show vertical cross section diagrams used for explanation of application examples of the recording medium of the present invention. Figure 1 shows the recording process, Figure 2 shows the playback process, and Figure 3 shows the erasure process, respectively. Figures 4-5 are explanatory diagrams that show the state of the enclosure complex of the present invention at the aqueous phase interface.

1...Host molecule
2...Guest molecule
3...Hydrophilic group
4...Long-chain alkyl group
5...Base
6...X-ray
7...Dimer

8...Visible light

9...Ultraviolet [radiation]

10, 11...Enclosure complex

12, 13...Enclosed complex

14...Long-chain fatty acid

15...Hydrophobic group

16...Aqueous phase
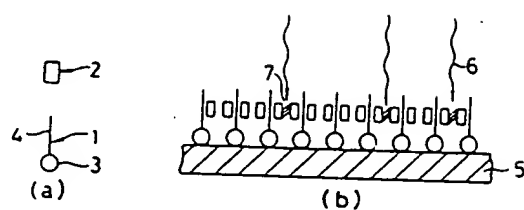
Figure 1
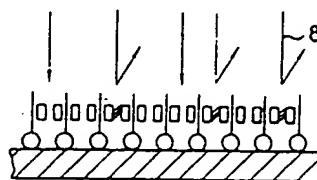
Figure 2
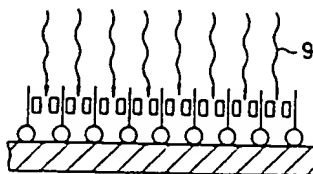
Figure 3

Figure 4

Figure 5

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明 細 書

1. 発明の名称

記録媒体

2. 特許請求の範囲

その分子内に親水性部位、疎水性部位及び包接部位を有するホスト分子と該ホスト分子に包接されるゲスト分子とからなる包接錯体の単分子膜又は単分子層累積膜を担体上に形成して記録層とし、前記ホスト分子とゲスト分子の錯体形成比が実質的に等モル比ではないことを特徴とする記録媒体。

3. 発明の詳細な説明

(1) 技術分野

本発明は、包接錯体の単分子膜、乃至単分子層累積膜の化学変化若しくは物理変化を利用して記録を行なう記録媒体に関する。

(2) 従来技術

従来、有機化合物を記録層とする記録媒体としては種々のものが知られている。

例えば、有機化合物を薄膜にして記録層として

用いる光記録媒体については、例えば特開昭56-16948号公報、特開昭58-125246号公報にも開示されている。いずれも有機色素を記録層とし、レーザビームにより記録再生を行なうレーザ記録媒体に関するものである。特に、特開昭58-125246号公報に開示された媒体は、

一般式（I）

$$\underset{R}{\underset{|}{\overset{X}{\underset{N}{\bigcirc\!\!\!\bigcirc}}}}\!\!-\!\!(CH\cdot CH)_3\!-\!CH\!\!-\!\!\overset{\bigcirc\!\!\!\bigcirc}{\underset{R}{}} \qquad (I)$$
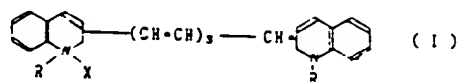
で表わされるシアニン系色素の薄膜を記録層とするものである。（I）式で表わされるシアニン系色素薄膜を回転塗布機などを用いて、1000Å以下の厚さ、例えば約300Åの厚さにプラスチック基板上に塗布し薄膜を形成する。膜内の分子分布配向がランダムであると、光照射に伴って膜内で光の散乱が生じ、微視的にみた場合各光照射の度に生ずる化学反応の度合が異なってくる。そこで記録媒体としては、膜内の分子分布、配向が一様になっていることが望ましく、またできる限り膜内

が薄いことが、記録の高密度化のために望調され る。しかしながら、蒸着による場合、膜厚においては 300Å程度が限界であり、膜内の分子分布、配向がランダムであることは解決しがたいことであった。

レジスト材料の一つとして量子効率が大でかつ優れた解像力を有するものとして提案されていたジアセチレン化合物累積膜が、レジスト材料のみならず、得関電気-光学デバイス、電気-音響デバイス、圧・焦電デバイス等にも応用されることが、特開昭56-42223号公報、特開昭56-43220号公報などに示されている。

近年においては、ジアセチレン化合物累積膜の製造方法の改良について特開昭58-111329号公報に示されている。かかる方法にて製造された基板上のジアセチレン化合物累積膜は紫外線を照射することにより重合させてジアセチレン化合物重合膜を作り、或はマスキングして紫外線を照射し選択的に重合させ、未重合部分を除去して図形を作り、得関光学デバイスや集積回路素子として使用される。

しかし、これらはいずれもジアセチレン化合物に限るものであり、得関光学デバイスとして使用するときに、一度記録したものの熱的安定性については述べられていない。

一方、上述欠点を解決すべく、分子内に親水基、疎水基及び少なくとも1個の不飽和結合を有する1種類の光重合性モノマーの単分子膜又は単分子層累積膜を基板上に形成して記録層としたことを特徴とする、反復使用可能な光記録媒体が特開昭58-130332号の光記録媒体に示されている。

これらのジアセチレン化合物累積膜にしても、光重合性オレフィンモノマーの単分子膜若しくは単分子層累積膜にしても、光反応性化合物に親水基、疎水基を導入して、直接基板上に担持させる製法を採用している。従って、種々の機能性膜を固体に作製することが困難なのに加えて、親水基、疎水基の導入に伴う光反応性の低下の恐れがあった。更には、より高度な高密度記録を行う際に重要となる、界面内の分子配向の制御につい

ても、極めて煩雑な操作が要求される問題があった。

かかる従来例の欠点を解消し、1)各種の機能性膜を比較的簡単に作製する方法、2)その際、機能性分子の付つ各種機能が、薄膜化した場合においても、喪失若しくは低下されることなく発現する様に固化する方法、更には、3)上記の薄膜化において、特別な操作を行うことなしに、膜構成分子が界面内方向に対して、高度の秩序構造を持って配向される方法を種々検討した結果、本発明を成すに至った。又、かかる成膜法を用いて、高密度、高耐熱度の記録媒体を、容易にかつ高品質に提供できるに至った。

(3) 発明の開示

本発明の目的は、外場により分子単位での化学又は若しくは物理変化を起す様な高密度記録媒体を提供することにある。

また、この様な分子単位での高密度記録を行うに際して重要な別子となる媒体面内での分子配向に関して、従来例よりも完全な媒体を提供する

ことにある。更には、上述記録媒体を製造するに当って、比較的簡単な操作変更により、様々な性質を有する媒体を提供することにある。

本発明の上記目的は、以下の本発明によって達成される。

その分子内に親水性部位、疎水性部位及び他分子との包接が可能な部位（包接部位）を有する分子（ホスト分子）と該ホスト分子に包接される別種の分子（ゲスト分子）とからなる包接錯体の単分子膜又は単分子層累積膜を担体上に形成して記録層とし、前記ホスト分子とゲスト分子の錯体形成比が実質的にも非モル比でないことを特徴とする記録媒体。

本発明の記録層を構成する物質は、分子内に親水性部位、疎水性部位及び他分子との包接が可能な部位を少なく共1ヶ所有する分子（これをホスト分子と呼ぶ）と該ホスト分子に包接される別種の分子（これをゲスト分子と呼ぶ）の二種の分子からなる。かかるホスト分子とゲスト分子とからなる包接錯体の単分子膜、乃至単分子層累積膜を

体として形成することにより、本発明の記録媒体が形成される。但し、これら二種類の分子の内、どちらか一方、若しくは、両方が、光、熱、電気、電気等の外場により、化学変化若しくは物理変化を起こすことが必要である。即ち、本発明における記録媒体は、前述の化学変化や物理変化を利用して記録を行なう。

本発明に用いられるホスト分子としては、上述のごとく、分子内の適当な位置に親水性部位、疎水性部位及び少なく共1ヶ所の包接分子との包接錯体を形成可能な部位を有し、ゲスト分子と定量的に下モル比でない包接錯体を形成する分子であれば広く使用することができる。分子内に親水性部位や疎水性部位を形成し得る構成要素としては、一般に広く知られている各種の親水基や疎水基等が代表的なものとして挙げられる。包接分子との包接錯体を形成し得る部位は、水酸基、カルボニル基、カルボキシル基、エステル基、アミノ基、ニトリル基、チオアルコール基、イミノ基等の導入によって形成される。このようなホスト分子

と、一般式（35）〜（36）で表される水酸基を持つホスト分子を例として、以下に具体的に説明する。

$$R_1-C-C \equiv C-C \equiv C-C-R_2 \qquad (35)$$

$$R_1 \underset{HO}{\overset{HO}{\diagdown}} R_2 \qquad (36)$$
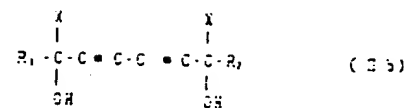
（ここで、X=H または C_6H_5 である。）

すなわち、分子内に親水性部位および疎水性部位を有するとは、例えば上式において R_1 基及び R_2 基の何れか一方に親水性部位が存在し、他方に疎水性部位が存在するか、R_1 基及び R_2 基が両基以外の残りの基との関係において共に親水性、若しくは疎水性を示すことを言う。R_1 基及び、R_2 基の構造に関して、疎水性部位を導入する場合には特に炭素原子数 5〜30 の長鎖アルキル基が、又親水性部位を導入する場合には特に炭素原子数 1〜30 の脂肪酸が望ましい。

本発明におけるホスト分子を更に具体的に示せば、ジアセチレンジオール誘導体 (No.7〜No.12、No.22〜No.27)、ハイドロキノン誘導体 (No.13〜No.15、No.28〜No.30)等が利用し得るものとして挙げられる。尚、以下の例におけるmは正の整数を、Zは、-CH₃または-COOHを、Phは、-C₆H₅を示すものとする。

（ジアセチレンジオール誘導体の例）

No.7

$$CH_3-(CH_2)_m-C-C \equiv C-C \equiv C-C-(CH_2)_n-COOH$$

$$30 \geq m+n \geq 9, \quad n \geq 0$$

No.8

$$CH_3-(CH_2)_m-\overset{Ph}{\underset{OH}{C}}-C \equiv C-C \equiv C-\overset{Ph}{\underset{OH}{C}}-(CH_2)_n-COOH$$

$$30 \geq m+n \geq 9, \quad n \geq 0$$

No.9

$$CH_3-(CH_2)_m-O-\bigcirc-\overset{H}{\underset{OH}{C}}-C \equiv C-C \equiv C-\overset{H}{\underset{OH}{C}}-\bigcirc-O-(CH_2)_n-COOH$$

$$30 \geq m+n \geq 5, \quad n \geq 1$$

No.10

$$CH_3-(CH_2)_m-O-\bigcirc-\overset{Ph}{\underset{OH}{C}}-C \equiv C-C \equiv C-\overset{Ph}{\underset{OH}{C}}-\bigcirc-O-(CH_2)_n-COOH$$

$$30 \geq m+n \geq 5, \quad n \geq 1$$

No.11

$$CH_3-(CH_2)_m-O-\langle\bigcirc\rangle-\underset{OH}{\overset{H}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{H}{C}}-\langle\bigcirc\rangle-(CH_2)_n-COOH$$

$30 \geqq m + n \geqq 5, \quad n \geqq 0$

No. 12

$$CH_3-(CH_2)_m-O-\langle\bigcirc\rangle-\underset{OH}{\overset{Ph}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{Ph}{C}}-\langle\bigcirc\rangle-(CH_2)_n-COOH$$
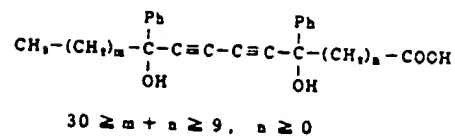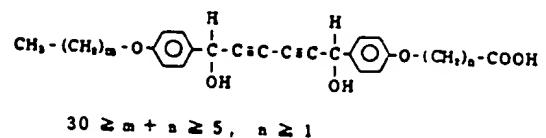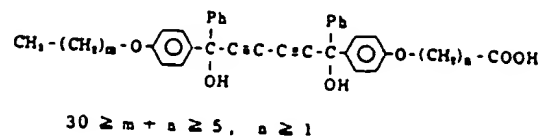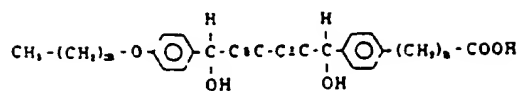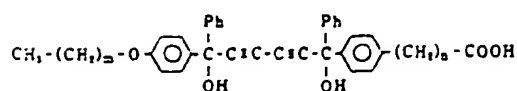
$30 \geqq m + n \geqq 5, \quad n \geqq 0$

（ハイドロキノン誘導体の例）

No. 13
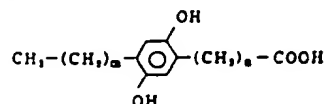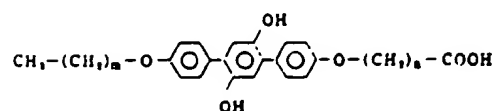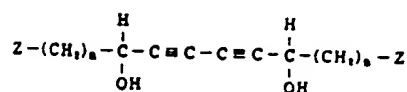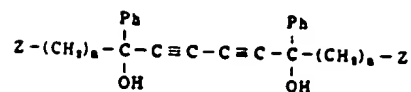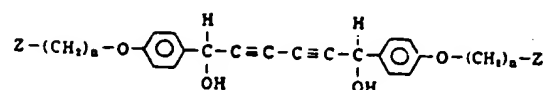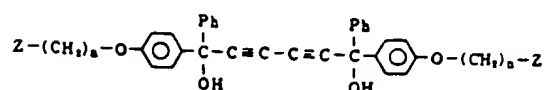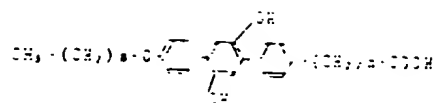
$$CH_3-(CH_2)_m-\langle\bigcirc\rangle\overset{OH}{\underset{OH}{}}-(CH_2)_n-COOH$$

$30 \geqq m + n \geqq 13, \quad n \geqq 0$

No. 14

$$CH_3-(CH_2)_m-O-\langle\bigcirc\rangle-\langle\bigcirc\rangle\overset{OH}{\underset{OH}{}}-\langle\bigcirc\rangle-O-(CH_2)_n-COOH$$

No. 15

$$CH_3-(CH_2)_m-O-\langle\bigcirc\rangle\overset{OH}{\underset{OH}{}}-\langle\bigcirc\rangle-(CH_2)_n-COOH$$

$30 \geqq m + n \geqq 3, \quad n \geqq 0$

（ジアセチレンジオール誘導体の例）

No. 22

$$Z-(CH_2)_n-\underset{OH}{\overset{H}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{H}{C}}-(CH_2)_n-Z$$

$30 \geqq n \geqq 3$

No. 23

$$Z-(CH_2)_n-\underset{OH}{\overset{Ph}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{Ph}{C}}-(CH_2)_n-Z$$

$30 \geqq n \geqq 3$

No. 24

$$Z-(CH_2)_n-O-\langle\bigcirc\rangle-\underset{OH}{\overset{H}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{H}{C}}-\langle\bigcirc\rangle-O-(CH_2)_n-Z$$

$30 \geqq n \geqq 1$

No. 25

$$Z-(CH_2)_n-O-\langle\bigcirc\rangle-\underset{OH}{\overset{Ph}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{Ph}{C}}-\langle\bigcirc\rangle-O-(CH_2)_n-Z$$

$30 \geqq n \geqq 1$

No. 26

$$Z-(CH_2)_n-\langle\bigcirc\rangle-\underset{OH}{\overset{H}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{H}{C}}-\langle\bigcirc\rangle-(CH_2)_n-Z$$

$30 \geqq n \geqq 1$

No. 27

$$Z-(CH_2)_n-\langle\bigcirc\rangle-\underset{OH}{\overset{Ph}{C}}-C\equiv C-C\equiv C-\underset{OH}{\overset{Ph}{C}}-\langle\bigcirc\rangle-(CH_2)_n-Z$$

$30 \geqq n \geqq 1$

（ハイドロキノン誘導体の例）

No. 28

$$Z-(CH_2)_n-\langle\bigcirc\rangle\overset{OH}{\underset{OH}{}}-(CH_2)_n-Z$$

$30 \geqq n \geqq 5$

No. 29

Z-(CH₂)ₙ-O-⬡-⬡-O-(CH₂)ₙ-Z

(with OH, HO substituents)

30 ≧ n ≧ 1

No. 30

Z-(CH₂)ₙ-⬡-⬡-(CH₂)ₙ-Z

(with OH, OH substituents)
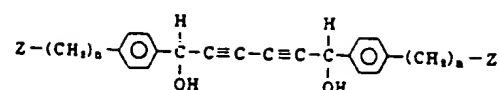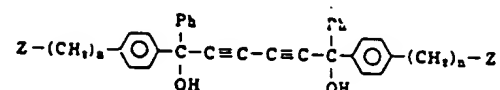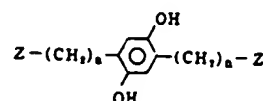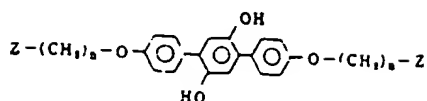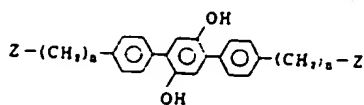
30 ≧ n ≧ 1

—以上挙げた化合物はゲスト分子に反応アルキル
基や反応カルボノ離子を履良させて関本性の結水
元を導入した点を除けばそれ自体既出の化合物で
あり、又、反応アルキル基等で修飾されていない
ホスト分子が、種々のゲスト分子と結晶性の包接
結体を形成する点に関しても、日本化学会法No.2
233貢・242貢（1983年）に述べられている。

これらホスト分子と包接錯体を作り得るゲスト
分子としては、一般に、ホスト分子と強い水素結
合を形成し得る分子が望ましい。従って、先に述
べたごとく、ホスト分子が包接部位として水酸基を
有する場合には、ゲスト分子として、アルデヒ
ド、ケトン、アミン、スルフォキシド等を挙げる
ことができる。また、ゲスト分子としては他に、
各種ハロゲン化合物、或いはπ-電子系化合物、
即ちアルケン、アルキン、及びアレーン等を選ぶ
もできる。何れにせよ、形成される包接錯体が
希望の室形成機能を示す構造を有する分子が選ば
れる。

—下、各種機能別に利用可能なゲスト分子の具

体例を示す。

(1) ゲスト分子の二量化反応を用いた光記録媒体
に利用し得るゲスト分子の具体例としては、オ
レフィン化合物（No.31～No.34）、ジオレフィ
ン化合物（No.35～No.38）、アノ・ラセノ誘導
体（No.39）、2-アミノピリジニウム（No.41）
等。

〔オレフィン化合物の例〕

No. 31
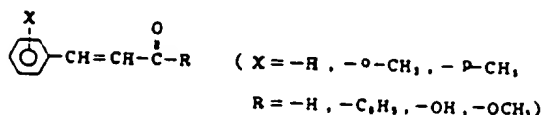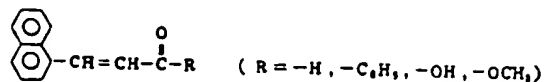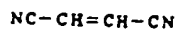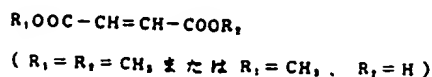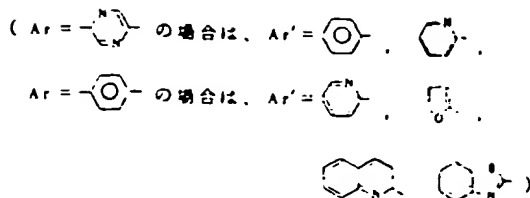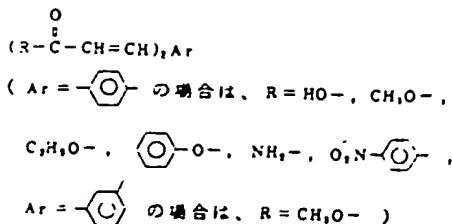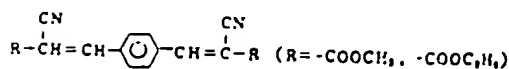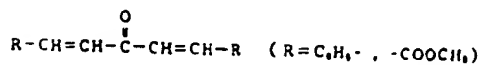
⬡-CH=CH-C(=O)-R   (X=-H , -o-CH₃, -p-CH₃
R=-H , -C₆H₅, -OH, -OCH₃)

No. 32

⬡⬡-CH=CH-C(=O)-R   (R=-H , -C₆H₅, -OH, -OCH₃)

No. 33

NC-CH=CH-CN

No. 34

R₁OOC-CH=CH-COOR₂

(R₁=R₂=CH₃ または R₁=CH₃ , R₂=H)

〔ジオレフィン化合物の例〕

No. 35

Ar'-CH=CH-Ar-CH=CH-Ar'

（ Ar = -◯-N の場合は、 Ar' = ◯ , ◯N- ,

Ar = -◯- の場合は、 Ar' = ◯N , ◯O ,

◯◯N- , ◯N-R ）

No. 36

$(R-\overset{O}{\overset{\|}{C}}-CH=CH)_2 Ar$

（ Ar = -◯- の場合は、R = HO- , CH₃O- ,

C₂H₅O- , ◯-O- , NH₂- , O₂N-◯- ,

Ar = -◯- の場合は、R = CH₃O- ）

No. 37

$R-CH=CH-◯-CH=\overset{CN}{\underset{}{C}}-R$ （R = -COOCH₃ , -COOC₂H₅）

（上にCN）

No. 38

$R-CH=CH-\overset{O}{\overset{\|}{C}}-CH=CH-R$ （R = C₆H₅- , -COOCH₃）

（アントラセン誘導体の例）

No. 39

（R = CH₃ , CHO- , -COOC₂H₅ , Br- ）

（アクリジニウム誘導体の例）

No. 40

（ R = -H , -CH₃ , -C₂H₅ , X⁻ = I⁻ , Br⁻ , Cl⁻ ）

（2-アミノピリジニウム）

No. 41

（ X⁻ = Cl⁻ , Br⁻ , I⁻ ）
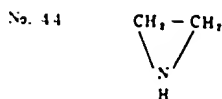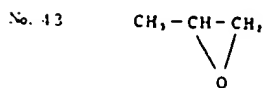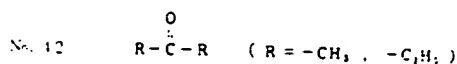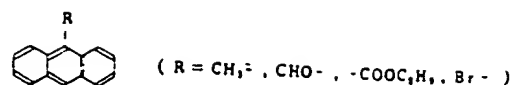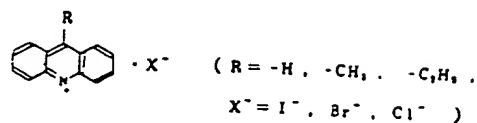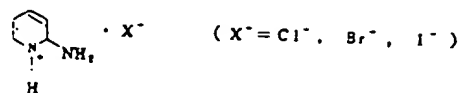
(2) ゲスト分子の昇華を利用した記録媒体に利用し得るゲスト分子の具体例としては、ケトン（No. 42）、1,2-エポキシプロパンなどのエポキシド（No. 43）、エチレンイミン（No. 44）、

ベンゼン（No. 45）、ジーエチルノクノ、……なとの塩化物（No. 45, No. 47, ……、……なとの臭化物（No. 48）。

No. 42 $R-\overset{O}{\overset{\|}{C}}-R$ （R = -CH₃ , -C₂H₅ ）

No. 43 $CH_3-CH-CH_2$ （下に O 環）

No. 44 CH_2-CH_2 （下に N-H 環）

No. 45 ◯

No. 46 CH₂Cl₂

No. 47 CHCl₃

No. 48 CH₃Br
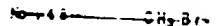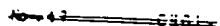
このようなホスト分子およびゲスト分子から成る包接錯体の単分子膜または単分子層累積膜を作製する方法としては、例えばI.Langmuirらの開発したラングミュア・ブロジェット法（LB法）を用いる。LB法は、例えば分子内に親水基と疎水基を有する構造の分子において、両者のバランス（両親媒性のバランス）が適度に保たれているとき、分子は水面上で疎水基を上に向けて単分子の層になることを利用して単分子膜または単分子間の累積膜を作製する方法である。水面上の単分子層は…次元系の特徴をもつ。分子がまばらに散開しているときは、一分子当り面積Aと表面圧πとの関

…に反して気体膜の如く、

$$A = RT$$

の法則のうち、"気体膜"となる。ここに、Rはガスノマン定数、Tは絶対温度である。Aを十分小さくすれば分子間相互作用が増より二次元固体の"凝縮膜（または固体膜）"になる。凝縮膜はガラス基板などの種々の材質や形状を有する固体の表面へ一層ずつ移すことができる。この方法を用いて、本発明のゲスト分子を包接するホスト分子の単分子膜（これを単独体分子膜と呼ぶことにする）、もしくは単独体分子膜累積膜の具体的な製法としては、例えば以下に示すA～Eの5法を挙げることができる。

［A］目的とする包接錯体のホスト分子とゲスト分子とを有機に溶解し、これを水相上に展開させて包接錯体を膜状に析出させる。この場合、ホスト分子の構造がNo.1～No.15に示したような分子の両端に親水性部位（カルボニル基）と疎水性部位（アルキル基）を有するものであれば、水相上に析出する包接錯体はゲスト分子の親水性より…

…硫水性のいかんにかかわらず、ホスト分子の親水性部位を水相に向けた状態で水相上に展開する。一方、ホスト分子がNo.16～No.30に示した構造をとる場合、分子の両端が疎水性部位のみで構成される2・-CHは、水相上に析出する包接錯体は、ゲスト分子の親水性部位を水相に向けた第4図に示すような状態で水相上に展開する。又、分子の両端が親水性部位のみで構成される2・-COOHでは水相上に形成される包接錯体は、ホスト分子の親水性部位を水相に向けた第5図に示すような状態で水相上に展開する。

次にこの析出物が水相上を自由に拡散して圧がかりすぎないように仕切板（または浮子）を設けて展開面積を制限して膜物質の集合状態を調御し、その集合状態に比例した表面圧口を得る。この仕切板を動かし、展開面積を縮少して膜物質の集合状態を調御し、表面圧を徐々に上昇させ、累積膜の製造に適する表面圧口を設定することができる。この表面圧を維持しながら静かに清浄な担体を垂直に上下させることにより単独体分子膜が担…

…体上に移しとられる。単独体分子膜は以上で製造されるが、単独体分子膜累積膜は前記の操作を繰り返すことにより所望の累積度の単独体分子膜累積膜が形成される。

単独体分子膜を担体上に移すには、上述した垂直浸せき法の他、水平付着法、回転円筒法などの方法による。水平付着法は担体を水面に水平に接触させて移しとる方法で、回転円筒法は、円筒型の担体を水面上に回転させて単独体分子膜を担体表面に移しとる方法である。前述した垂直浸せき法では、表面が疎水性である担体を水面を横切る方向に水中から引き上げるとホスト分子の疎水基が担体側に向いた単独体分子膜が担体上に形成される。前述のように担体を上下させると、各行程ごとに1枚ずつ単独体分子膜が積み重なっていく。成膜分子の向きが引上げ行程と浸せき行程で逆になるので、この方法によると各層間はホスト分子の疎水基と疎水基、ホスト分子の親水基と親水基が向かい合うY型膜が形成される。それに対し、水平付着法は、担体を水面に水平に接触させ…

…て移しとる方法で、ホスト分子の疎水基が担体側に向いた単独体分子膜が担体上に形成される。この方法では、累積しても、成膜分子の向きの交代はなく全ての層において、疎水基が担体側に向いたX型膜が形成される。反対に全ての層において親水基が担体側に向いた累積膜はZ型膜と呼ばれる。

回転円筒法は、円筒型の担体を水面上を回転させて単分子膜を担体表面に移しとる方法である。単分子膜を担体上に移す方法は、これらに限定されるわけではなく、大面積担体を用いる時には、担体ロールから水相中に担体を押し出していく方法などもとり得る。また、前述した親水基、疎水基の担体への向きは反問であり、担体の表面処理子によって変えることもできる。

以上の成膜過程において膜物質の面内方向の配向性調御は従来、主として表面圧の調御に依ってなされていた訳であるが、膜物質が余程単純な構造の化合物、例えば直鎖脂肪酸子の場合を除き、高い異序性を得ることは極めて困難であった。従…

本発明においては、包接錯体を開物質に用いそこで、あい旋作性を持つ物を比較的簡単に得ることができる。即ち、水面上に包接錯体が開状に析出した時点で、水素結合やファン・デル・ワールス力等に則ってホスト分子ーゲスト分子間、ゲスト分子ーホスト分子間、ゲスト分子ーゲスト分子間の立体的配置は固定され、各ホスト分子及びゲスト分子は結晶格子的規序性を持って配列する。又、ゲスト分子のみが磁性を持つ場合には、このゲスト分子への化学的修飾、即ち、磁性原子や磁性基の導入を行わないので、酸化に伴う磁性の低下は生じない。

[B] 水溶性を示すゲスト分子を水相に溶解させる。次にホスト分子を溶剤に溶解せしめてこれを水相上に展開させる。この時同時にホスト分子ーゲスト分子間で包接錯体形成が行われて開状に析出する。ホスト分子とゲスト分子の組み合わせ及びゲスト分子の成膜操作については[A]に示した方法に準ずる。

[C] 水溶性を示すゲスト分子を水相に溶解させ、次に、目的とする包接錯体のホスト分子とゲスト分子とを各個に溶解し、これを水相上に展開させて包接錯体を開状に析出させる。ゲスト分子とゲスト分子の組み合わせ及び以下の成膜操作については[A]に示した方法に準ずる。

[D] ホスト分子を各個に溶解しこれを水相中に展開させる。その後、密閉系の装置を用いて気相側、即ち装置内の空間をゲスト分子ガス雰囲気とする。この時、両所に気相側のゲスト分子を包接し、包接錯体が開状に析出する。この方法はゲスト分子が低沸点で気化し易い性質を持つ化合物、例えばアセトン等の場合、特に有効である。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操力については[A]に示した方法に順ずる。

[E] 密閉系の装置を用いて気相側、即ち装置内の空間をゲスト分子ガス雰囲気とする。次に目的とする包接錯体のホスト分子とゲスト分子とを各個に溶解し、これを水相上に展開させて包接錯体を開状に析出させる。ホスト分子とゲスト分子の組み合わせ及び以下の成膜操作については、[A]

に示した方法に準ずる。

以上の方法によって固体上に形成される単錯体分子間及び単錯体分子層累積間は高密度でしかも高度の規序性を有しており、これらの層で記録層を構成することによって、包接錯体の磁性に応じて光記録、熱的記録、電気的記録あるいは磁気的記録下の可逆な高密度で高解像度の記録磁性を有する記録媒体を得ることができる。

作成した単錯体分子層及び単錯体分子層累積間を記録媒体の記録層として用いる場合以下に示す様に各種の記録法が考えられる。

ゲスト分子の光二量化反応を用いた光記録法。例えばホスト分子にNo.7~15、No.22~30のいずれかと、No.31-38等の光二量性二重結合を有するゲスト分子とを組み合わせるとホスト分子／ゲスト分子の組成比(mol比)が1:2の包接錯体が形成される。この単錯体分子間、若しくは、単錯体分子層累積間にあるパターンに従ってガンマ線、X線、紫外線など重合に必要なエネルギーを供給しうる光を照射すると照射部位において

て図又に示すようにゲスト分子間で二量化反応がおこる。

$$
\begin{array}{ccc}
\begin{array}{c}
R_1 \quad\quad R_1 \\
| \quad\quad | \\
HC \quad\quad CH \\
| \quad\quad | \\
HC \quad\quad CH \\
| \quad\quad | \\
R_1 \quad\quad R_1
\end{array}
& \xrightarrow{h\nu} &
\begin{array}{c}
R_1 \quad\quad R_1 \\
| \quad\quad | \\
HC - CH \\
| \quad\quad | \\
HC - CH \\
| \quad\quad | \\
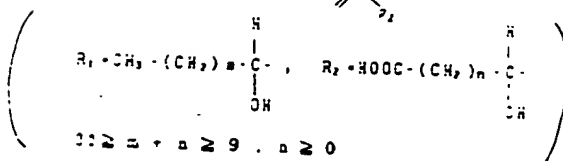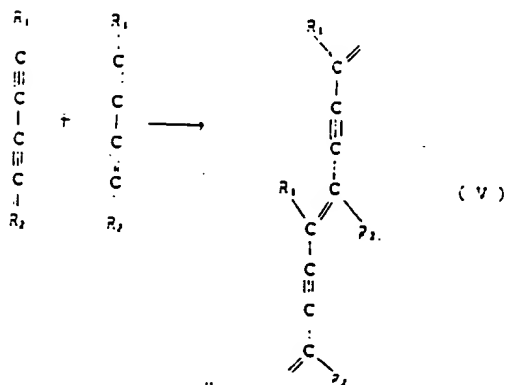R_1 \quad\quad R_1
\end{array}
\end{array}
\quad (\exists)
$$
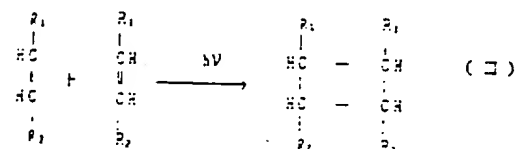
これらの反応は互いに隣接する不飽和結合の距離が4Å以下のときおこり得るものであるが、先に述べた様な方法で作成された単錯体分子間又は、単錯体分子層累積間では、二量化物が容易に得られるのみならず、二量化反応に伴って生成が考えられる各種の異性体若しくは構造体の唯一種しか生成されない。即ち、包接錯体層におけるゲスト分子間の立体配列は、極めて堅密としている。また、二量化した後は、磁場下でも解重合は起らず、非照射部位は単量体のままであるので、第1図に示すように、或るパターンに従った記録が成される。

記録された情報の読み取りは例えば可視光の照射によって行なう。すなわち、重合によって単量

体作の共役系が崩れるので、可視光の吸収波長に
変化をきたす。最大吸収波長は短波長側にシフト
するので、吸収スペクトル変化を読みとることに
より情報の再生が行なわれる（第2図）。

再生は、可視光による吸収スペクトル変化の読
み取り以外にも、単量体時と二量化後の体積変化
をシュリーレン法により読みとることも可能であ
る。この方法は、単量体時と二量化後の体積変化
の大きい構造を有する化合物の単量体分子膜また
は単量体分子層累積膜のときには特に適してい
る。また、単量体分子膜または単量体分子層累積
膜を基板の上に直接ではなく、基板上にSe、ZnO、
CdSなどの光導電体層を形成し、その上に単量体
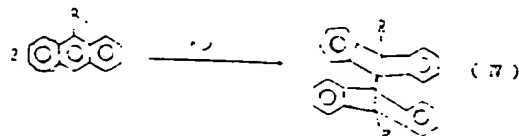分子膜または単量体分子層累積膜を形成すること
により、単量体と二量体の受光度の差を電気的に
読み取ることも可能である。

二量体はシクロブタン環に基づく、波長270nm
の吸収をもつが、この波長270nmの紫外光を照射
することによって二量体は元の単量体二分子に戻
る。従って一度記録された情報の消去が可能とな

（第3図）

なお、単性のゲスト分子としてアントラセン
誘導体No.33の如き化合物を用いる事もできる。
この場合光二量化反応は下式に従って進行する。

$$\text{(IV)}$$

又、ホスト分子としてNo.7を用いた場合に
は、X線、ガンマ線、紫外線等の重合に必要なエ
ネルギーを供給し得る光を照射すると、照射部位
に於いてIV式に示す様にホスト分子間で重合がお
こり、ポリジアセチレンが形成される。

$$\text{(V)}$$

$R_1 = CH_3-(CH_2)_m-C- \ , \quad R_2 = HOOC-(CH_2)_n-C-$

$m \geqq 9, \ n \geqq 0$

従って、単量体分子膜若しくは単量体分子層累
積膜に全面露光することにより、基板との付着力
を飛躍的に増大せしめることが可能である。特に
耐薬品（耐溶例）性が増大する。かかる、全面露
光により、ゲスト分子が光二量性を示す場合には
ゲスト分子も、二量化してしまうが、これを光記
録媒体として用いる際には、前述例とは逆に

ターンに従ってシクロブタン環の吸収波長に等し
い波長の光（紫外光）を照射して解重合させるこ
とにより記録乃至表示が出来る次である。

以上述べた光記録媒体に於いて膜厚は、特に
100～3000Åのものが好ましい。
2. ゲスト分子の昇華を利用した記録媒体
例えばホスト分子としてNo.7～15、No.22等の
何れかと、No.42-48等のゲスト分子を組合わせ
ると、ホスト分子対ゲスト分子の組成比（mol
比）が1:2の包接錯体が形成される。この単量
体分子膜若しくは単量体分子層累積膜にあるパ
ターンに従ってこれらゲスト分子が包接錯体より
離脱して気化するに十分なエネルギーを有する
レーザ光や電子線等を照射すると非照射部位に於
いては、ゲスト分子はホスト分子に包接されたま
まであるので上記パターンに従った記録が成され
たことになる。

記録された情報の読み取りは、ゲスト分子とし
てNo.42、を用いた場合にはこれらの化合物が持
つカルボニル基に基づく紫外光吸収の有無を読み

ることにより促される。又、シード光の電子線照射前後の膜の構造変化をシュリーレン法により読み取ることもできる。この方法は、ゲスト分子として No.42〜48 を用いた場合にも有効である。

又、No.41 を含む甲鎖体分子間乃至甲鎖体分子層累積膜を Se、ZnO、CdS等の光導電体層上に形成することにより包接錯体活とゲスト分子のみの部位この受光度の差を電気的に読み取ることも可能である。

上記の記録媒体において膜厚は、特に 100〜1000Å のものが好ましい。

これら読開方法はその原理からも分る通り、々々に簡易な方法であり、上記のような優れた記録安定を有する記録媒体を低コストで提供することができる。

上に述べた、本発明における甲鎖体分子層または甲鎖体分子累積膜を形成する担体は特に限定されないと、担体表面に界面活性物質が付着していると、甲鎖体分子層を水面から移しとる時に、甲鎖体分子間が乱れ良好な甲鎖体分子層または甲鎖

体分子層累積膜ができないので担体表面が清浄なものを使用する必要がある。使用することのできる担体の例としては、ガラス、アルミニウムなどの金属、プラスチック、セラミックなどが挙げられる。

担体上の甲鎖体分子層または甲鎖体分子層累積膜は、十分に強く固定されており担体からの剥離、剥布を生じることはほとんどないが、付着力を強化する目的で担体と甲鎖体分子層または甲鎖体分子層累積膜の間に接着層を設けることもできる。さらに甲鎖体分子層形成条件例えば水相の水素イオン濃度、イオン種、水温、担体上げ下げ速度あるいは表面圧の選択等によって付着力を強化することもできる。

甲分子層または甲分子層累積膜の上に保護層を設けることに、甲分子層または甲分子層累積膜の化学的安定性を向上させるためには、好ましいことであるが、成膜分子の選択によって保護層は設けても設けなくてもよい。

以下に本発明の実施例を示して更に具体的に説

別する。No.43〜No.53の化合物は、第1表に示す。

実施例 1

ゲスト分子の光二量化反応を用いた光記録媒体 (i)

テスト分子として No.43 及び49 のジアセチレンジオールと、ゲスト分子としてカルコンをモル比 1：2 の割合でクロロホルムに溶かした後、pH6.5、塩化カドミウム濃度 4×10⁻⁴ M の水相上に展開させた。展開のクロロホルムを蒸発除去後、表面圧を 35dynes/cm まで高めて、包接錯体を膜状に析出させた。この後、表面圧を一定に保ちながら、表面が十分に清浄で撥水性となっているガラス基板を上下速度 7cm/min にて水面を横切る方向に静かに上下させ、甲鎖体分子間を基板上に移し取り、甲鎖体分子層及び 3、5、9、15、19 層に累積した甲鎖体分子間累積膜を記録層とする光記録媒体を製造した。この累積行程において基板を水相から引きあげる都度に、30分間以上放置して、基板に付着している水分を蒸発除去し

た。なお成膜装置としては、英国 Joyce社製の Langmuir-Trough を使用した。

作成した光記録媒体にパターンに従って、X線照射を行い、式⑪に示すゲスト分子の二量化反応を行ない情報を記録した。分子オーダーの高密度記録が可能であった。

カルコン　　　　　　　　　　　　　　　（⑪）
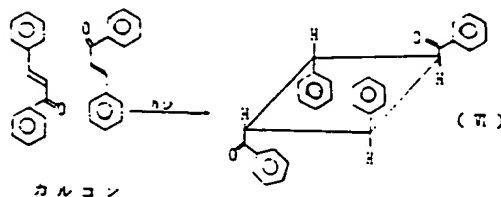
記録の再生はゲスト分子の二量化に伴う波長 380nm〜420nm付近の吸収変化を読み取る事により行った。次いで波長 270 nm の紫外光を 1 時間照射したところ、解重合がおこり、記録が消去がされた。

実施例 2〜12

実施例1のカルコンの代わりにゲスト分子とし

て No.3〜No.29の化合物を用いた場合も同様の
結果を得た。（実施例2〜9）

又、ゲスト分子をカルコンとし、ホスト分子を
No.53〜No.52とした場合にも、実施例1と同
様、光による記録、再生、更には、記録の消去が
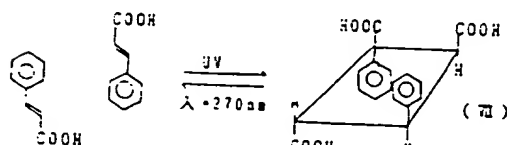可能であった。（実施例10〜12）

実施例13〜24

ゲスト分子の光二量化反応を用いた光記録媒体
（2）

実施例1〜12で述べた各光記録媒体を先づ高圧
水銀灯により全面露光せしめて、全てのゲスト分
子を二量化した。かかる媒体に二量化に伴って生
成されたシクロブタン環の吸収極大に相当する波
長273nm付近の紫外光をパターン状に照射し、ゲ
スト分子を解重合し情報を記録した。分子オー
ダーの記録が可能であった。記録の再生は、ゲス
ト分子の解重合に伴う波長380〜420nm付近の吸
収変化を読み取る事により行った。更に再び高圧
水銀灯を用いて上記記録媒体を全面露光すること
により、記録を消去、即ち、全てのゲスト分子を二

に伴う波長380〜420nm付近の吸収変化を読み取
る事により行った。

更に再び高圧水銀灯を用いて上記記録媒体を全面
露光することにより記録を消去することが可能で
あることを確認した。なお一度高圧水銀灯で全面
露光した本記録媒体を、アルコール中に約30秒間
浸漬した後、上記方法により情報の記録／再生を
行ったが、特に問題点はなかった。即ち、ホスト
分子を重合させる事により既記録媒体の化学的強
度が大となることが確認された。

実施例26、27

ホスト分子として No.53のジアセチレンジオ
ール、ゲスト分子としてアントラアルデヒドをモ
ル比1：2の割合でクロロホルムに溶かし、実施例
1と同様に操作により単錯体分子膜及びこれを
5、9、15、31層に累積した単錯体分子層累積膜
を記録層とする光記録媒体を製品した。

作製した光記録媒体にパターンに従ってX線照
射を行ない、式（Ⅶ）に示すゲスト分子の二量化
反応を行ない情報を記録した。分子オーダーの記

量化することが可能であることを確認した。

実施例25

ゲスト分子の光二量化反応を用いた光記録媒体
（3）

ホスト分子として No.53のジアセチレンジオ
ール、ゲスト分子としてケイ皮酸を用いて、実施例
1と同様の操作により単錯体分子膜及び、これを
3、5、9、15、19層に累積した。単錯体分子層
累積膜を記録層とする光記録媒体を製品した。次
に高圧水銀灯を用いて、これらの膜を全面露光し
て、ゲスト分子を二量化（式Ⅶ）、ホスト分子を
重合（式Ⅴ）させた後、パターンに従って、波長
270nmの紫外光を照射して、ゲスト分子を解重合
させて情報を記録した。分子オーダーの記録が可
能であった。

記録の再生は、二量化したゲスト分子の解重合

記が可能であった。記録の再生はゲスト分子の二
量化に伴う波長370〜390nm付近の吸収変化を読
み取る事により行った。次いで、波長313nmの紫
外光を1時間照射したところ解重合が起こり、記
録の消去が可能であることを、確かめた。

No.41のアントラセン誘導体を用いた場合にも
同様の結果を得た。（実施例27）

実施例28

ゲスト分子の昇華を利用した記録媒体(1)

ホスト分子として、No.49のジアセチレンジ
オールをクロロホルムに溶かした後、pH6.5、塩
化カドミウム濃度4×10⁻⁴ Mの水相上に展開させ
た。母液のクロロホルムを蒸発除去させた後、系
の気相側をアセトンで飽和させた。このアセトン
不用気下、表面圧を35dynes/cmにまで高めて包層
錯体を膜状に折出させた後、気相側のアセトンを
空気若しくは窒素で置換した。次いで、表面圧を
一定に保ちながら、表面が十分に清浄なガラス基
板を上下速度2cm/minで水面を横切る方向に静か
に上下させ、単錯体分子膜を基板上に移しとり、

甲鎖体分子膜及び3，5，9，15，19，43，60，
番層に累積した甲鎖体分子層累積膜を記録層とす
る記録媒体を製造した。この累積過程において、
基板を水面から引き上げる温度に30分間以上放
置して基板に付着している水分を再蒸発した。
圧縮装置としては、英国Joyce社製のLangmuir
Trough 4 を使用した。

次に炭酸ガスレーザ又は赤外線レーザを用いて作成
した記録媒体にパターンに従ってレーザ光を照射
したところ、照射部位だけゲスト分子、即ちアセ
トン分子が、気化除去され、その部分の吸収スペ
クトル強度（λmax=280nm）が減少し、情報の記録
が成された。分子オーダーの記録が可能であっ
た。又、ゲスト分子の有無をシュリーレン法を用
いて読みとることによる記録再生方法も可能で
あった。この該記録媒体をアセトン気流中に1時
間放置したところ、アセトンの除去された部位に
再びアセトンが包接され、記録が消去されると共
に、再記録が可能であった。この記録消去一再記
録のプロセスは少なくとも数十回の使用に耐え、

とする記録媒体を製造した。

次に炭酸ガスレーザは赤外線レーザを用いて作成
した記録媒体にパターンに従ってレーザ光を照射
したところ、照射部位だけ、ゲスト分子、即ちク
ロロホルムが、気化除去され記録が成された。分
子オーダーの記録が可能であった。このゲスト分
子の部分的除去に伴う膜の形状変化をシュリーレ
ン法を用いて読みとることにより情報の再生が可
能であった。該記録媒体をクロロホルム気流中に
1時間放置したところ、クロロホルム分子が再包
接され、記録が消去されると同時に再記録が可能
であった。この記録消去一再記録のプロセスは、
少なくとも数十回の使用に耐え、反復使用が可能
であることを確認した。

なおゲスト分子及び展開媒体として、ベンゼン
（No.45，実施例36）、ジクロルメタン（No.46，実
施例37）を用いた場合にも同様の結果を得た。

実施例38～43

ゲスト分子の昇華を利用した記録媒体（3）

ホスト分子として No.49～ No.52、ゲスト分子

反復使用が可能であることを確認した。

実施例29～31

実施例28のゲスト分子 No.43のかわりに No.50
～ No.52を用いた場合にも実施例28と同様の結果
が得られた。

実施例32～37

ゲスト分子の昇華を利用した記録媒体（2）

ホスト分子として No.49～ No.52を用い、クロ
ロホルムに溶かした後、pH6.5、塩化カドミウム
濃度 4×10⁻⁴ M の水面上に展開させた。この際、
系の気相側をクロロホルムでほぼ飽和させた。各
層（液側）のクロロホルムがほぼ気化するのを
待って（約5分）、表面圧を35dynes/cmにまで高
めて包接媒体を膜状に析出させた後、気相側のク
ロロホルムを空気、若しくは真空で置換した。次
いで、表面圧を一定に保ちながら表面が十分に清
浄なガラス基板を上下速度、2cm/min にて水面を
横切る方向に静かに上下させ、甲鎖体分子膜を基
板上に移しとり、甲鎖体分子膜及び3，5，9，
15，19層に累積した甲鎖体分子層累積膜を記録層

として1,2-エポキシプロパン（No.43）を用いて実
施例26と同様にして甲鎖体分子膜乃至、甲鎖体分
子層累積膜を記録層とする記録媒体を製造した
（実施例38～41）。この際、予め水相側に1,2-エ
ポキシプロパン（No.43）を 1～10M程度溶解させ
て、気相側のゲスト分子が、水中に拡散するのを
防止した。情報の記録、再生、及び消去の方法並
びに結果は実施例28と同様であった。

なお、ゲスト分子としてアセトン、エチレンイ
ミン（No.44）を用いた場合も同様の結果を得た。
（実施例42～43）。

実施例44～47

ゲスト分子の昇華を利用した記録媒体（4）

ホスト分子として No.49～ No.52、ゲスト分子
として臭化メチル No.48を用いて実施例26と同様
にして甲鎖体分子膜乃至甲鎖体分子層累積膜を記
録層とする記録媒体を製造した。情報の記録、再
生及び消去の方法並びに結果は実施例28と同様で
あった。

実施例48～54

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ゲスト分子の昇華を利用した記録媒体（5）

　ゲスト分子として No.53 を用い、ゲスト分子に No.42～No.46 を用いて電導体分子層乃至3,5,9層に実積した電導体分子層累積膜を作成した。この作成方法はゲスト分子の種類によって、互に異なり、実施例26～43に記した方法により作成した。かかる電導体分子層乃至電導体分子層累積膜を高圧水銀灯を用いて全面露光してホスト分子を重合させて記録媒体を製造した。

　得られた記録、再生、及び消去の方法ならびに結果は、実施例26或いは実施例28と同様であった。本方法によればホスト分子の基板付着力が、実施例26～43に比へて、増大する。従って記録媒体の化学的強度が相対的に大となり、反復使用回数を少なくとも 100回まで増大できることがわかった。
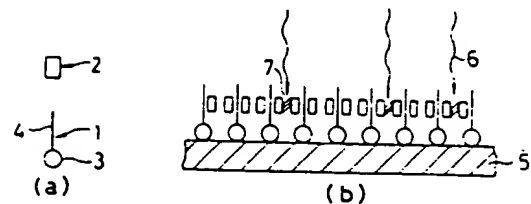
表：A

	基本骨格	
No.49	No.0	$m = 9$, $z = 2$
No.50	No.25	$Z-COOH$, $n = 2$
No.51	No.15	$m = 9$, $n = 2$
No.52	No.30	$Z-COOH$, $n = 4$
No.53	No.7	$m = 8$, $n = 8$

4.図面の簡単な説明

　第1図～第3図は、本発明に係る電気記録媒体の実施例を説明する断面面図であり、各々、第1図は電気消去記録入過程、第2図は再生過程、第3図は消去過程を示しており、第4図～第5図は本発明に係る包接媒体が水面上における状態を説明する説明図である。

1 … ホスト分子　　　2 … ゲスト分子
3 … 親水性部位
4 … 長鎖アルキル部位
5 … 基板
6 … 光線
7 … 二量化部位　　　8 … 可視光
9 … 赤外線
10, 11 … 包接部位
12, 13 … 複合層部位
14 … 長鎖脂肪酸部位
15 … 疎水性部位
16 … 水相

第 1 図

第 2 図

第 3 図

第 4 図

第 5 図